

PROCESS FOR PRODUCING PHENOL AND
METHYL ETHYL KETONE

5

Cross-reference to Related Applications

[0001] The present application claims the benefit of U.S. Provisional Patent Application Serial No. 60/447,526, filed February 14, 2003, pending.

10

Field of the Application

[0002] The present application relates to a process for producing phenol and methyl ethyl ketone (MEK). The product also may comprise acetone, acetophenone, and combinations of the foregoing.

15

Background

[0003] Phenol is an important chemical parent substance with a broad usage spectrum. For example, phenol is used to produce phenol resins, bisphenol A, caprolactam, adipic acid, alkyl phenols, and plasticizers.

20

[0004] In general, phenol is manufactured by oxidizing cumene to form the hydroperoxide of cumene, followed by cleavage of the cumene hydroperoxide with an inorganic acid such as sulfuric acid to form a cumene hydroperoxide cleavage product. The cumene hydroperoxide cleavage

25

product generally contains species such as phenol, acetone, α -methyl styrene (**AMS**), cumene, cumyl phenol (**CP**), dimethylbenzyl alcohol (**DMBA**), acetophenone (**AP**), AMS dimers (**AMSd**), tars and heavies, and inorganic acid such as sulfuric acid. Acetone, acetophenone, and phenol are the primary products in this group. Equimolar amounts of acetone and phenol generally are produced by this method.

30

35

[0005] Although acetone has a variety of uses, acetone generally is not in as high demand as phenol. MEK is a technically important ketone which is used, for example, as a lacquer and as a resin solvent. MEK is a high value ketone which can be produced if s-butylbenzene is used in the production of phenol (rather than cumene). The methods described to date for producing MEK as a co-

product in the production of phenol have not proven to be commercially viable.

[0006] Commercially viable methods are needed for producing controllable yields of phenol and MEK (and, if
5 desired, acetone) during the manufacture of phenol, particularly methods which are controllable to increase or decrease MEK yield, depending upon market demand.

Brief Description of the Drawings

[0007] Figure 1 is a block diagram of the process of the
10 present application.

[0008] Figure 2 is a schematic diagram of a preferred cleavage reactor system comprising a pipeline loop reactor and a plug flow reactor.

[0009] Figure 3 is a chart of the ratio of acetophenone to
15 total hydroperoxides achieved in a control with no added NH_3 , in experimental samples to which NH_3 was added as described in Example 2, and in a sample to which dry NH_3 was added at a ratio of 330:1 based on expected acid production.

[0010] Figure 4 is a chart of the ratio of (DMBA + EMBA)
20 to total hydroperoxides achieved in a control with no added NH_3 and in experimental samples to which NH_3 was added, as described in Example 2.

[0011] Figure 5 is a chart of the ratio of phenol to total
25 hydroperoxides achieved in a control with no added NH_3 and in experimental samples to which NH_3 was added, as described in Example 2.

Summary

[0012] The application provides a process for producing
30 controllable yields of a combination of products selected from the group consisting of (a) phenol and methyl ethyl ketone (MEK) and (b) phenol, acetone, and MEK. The process comprises:

35 feeding an oxidation feed to an oxidation reactor to produce an oxidation mixture, the oxidation feed comprising one or more alkylbenzenes selected from the group consisting of (a) a content of s-butylbenzene, and (b) a

combination of s-butylbenzene and cumene at a weight ratio of cumene to s-butylbenzene; exposing the oxidation mixture to oxidation conditions effective to produce an oxidation product stream comprising product hydroperoxides selected from the group consisting of (a) s-butylbenzene hydroperoxide, and (b) a combination of s-butylbenzene hydroperoxide and cumene hydroperoxide; cleaving the product hydroperoxides under cleavage conditions effective to produce a cleavage product comprising a combination selected from the group consisting of (a) phenol and MEK, and (b) phenol, acetone, and MEK; and, separating the cleavage product under separation conditions effective to separate a crude phenol fraction comprising phenol and a crude ketone stream selected from the group consisting of (a) a crude MEK stream and (b) a crude acetone/MEK stream comprising MEK and acetone; and, recovering one or more products selected from the group consisting of (a) an MEK product and (b) a combination comprising an MEK product and an acetone product.

[0013] The application also provides a process for producing controllable yields of phenol, acetone, and methyl ethyl ketone comprising:

feeding an oxidation feed to an oxidation reactor to produce an oxidation mixture, the oxidation feed comprising a combination comprising cumene and s-butylbenzene, wherein the amount of cumene is from greater than 15 wt.% to less than 30 wt.% relative to the content of s-butylbenzene; exposing the oxidation mixture to oxidation conditions effective to produce an oxidation product stream comprising s-butylbenzene hydroperoxide and cumene hydroperoxide; and,

cleaving the product hydroperoxides under cleavage
conditions effective to produce a cleavage
product comprising phenol, acetone, methyl
ethyl ketone;

5 separating the cleavage product under separation
conditions effective to separate a crude phenol
fraction comprising phenol and a crude ketone
stream comprising methyl ethyl ketone (MEK) and
acetone; and,

10 subjecting the crude ketone stream to ketone
separation conditions effective to produce an
acetone product and a methyl ethyl ketone
product.

[0014] The application also provides a process for
15 producing phenol, methyl ethyl ketone, and acetone
comprising:

feeding an oxidation feed comprising a weight ratio
of cumene:s-butylbenzene of from about 1:8 (or
12.5 wt.% cumene) to about 2:1 (or about 66.7
20 wt.% cumene) to an oxidation reactor to produce
an oxidation mixture,

exposing the oxidation mixture to oxidation
conditions effective to produce an oxidation
product stream comprising s-butylbenzene
25 hydroperoxide and cumene hydroperoxide;

cleaving the s-butylbenzene hydroperoxide and cumene
hydroperoxide under cleavage conditions
effective to produce a cleavage product
comprising phenol, acetone, and methyl ethyl
30 ketone;

separating the cleavage product under separation
conditions effective to separate a crude phenol
fraction comprising phenol and a crude ketone
stream comprising methyl ethyl ketone (MEK) and
35 acetone; and,

subjecting the crude ketone stream to ketone
separation conditions effective to produce an
acetone product and a methyl ethyl ketone
product.

Description

[0015] The present application relates to a process for producing a controllable product slate comprising phenol and methyl ethyl ketone (MEK). The product also may
5 comprise acetone, acetophenone, and combinations thereof at controllable yields.

[0016] The term "hydrocarbon" or "hydrocarbons," as used herein, refers to any mixture comprising one or more of cumene, s-butyl benzene, AMS, α -ethyl styrene (AES), 2-
10 phenyl-2-butene (2P2B), and combinations thereof.

Oxidation Zone

[0017] Referring to Fig. 1, the process comprises an oxidation zone 10 comprising one or more oxidation reactor(s). The oxidation reactor(s) may be batch
15 reactor(s) or continuous reactor(s). In a preferred embodiment, the oxidation zone 10 comprises a series of continuous reactors.

[0018] An oxidation feed is fed to the oxidation reactor(s). The oxidation feed comprises either (a) s-butylbenzene, or (b) a combination comprising an amount
20 of cumene and a content of s-butylbenzene. In the oxidation reactor(s), the oxidation feed is oxidized by molecular oxygen, preferably air, to produce an oxidation product stream. The oxidation product stream is
25 separated in the oxidation reactor(s) into an oxidation bottoms and an oxidation vapor overhead.

[0019] Where the oxidation feed is s-butylbenzene, the oxidation product stream comprises s-butylbenzene hydroperoxide, but typically does not comprise a
30 significant amount of cumene hydroperoxide. The operating conditions can be adjusted to coproduce more or less acetophenone (AP).

[0020] Where the oxidation feed comprises both cumene and s-butylbenzene, the oxidation product stream comprises s-butylbenzene hydroperoxide and cumene hydroperoxide at
35 high selectivity. The oxidation product stream also comprises certain major byproducts, including but not necessarily limited to acetophenone, di-methyl benzyl carbinol (DMBA), and ethyl methyl benzyl carbinol (EMBA).

Finally, the oxidation product stream may comprise minor by-products, including but not necessarily limited to di-cumyl peroxide, di-s-butylperoxide, cumyl s-butyl peroxide, formic acid, acetic acid, methanol, ethanol,
5 methyl hydroperoxide, ethyl hydroperoxide, phenol, acetone, and MEK.

[0021] In a preferred embodiment, the oxidation mixture comprises a weight ratio of cumene:s-butylbenzene of from about 1:8 to about 2:1. In percentage terms, the
10 foregoing ratios represent from about 12.5 wt.% cumene to about 66.7 wt.% cumene. In another embodiment, the amount of cumene is from greater than 15 wt.% to less than 30 wt.% relative to the content of s-butylbenzene.

[0022] Without limiting the claims to a particular
15 mechanism of action unless expressly stated in a claim, the predominate mechanism for the formation of the major and minor by-products (described previously) is believed to be the free radical decomposition of the s-butylbenzene hydroperoxide and (if present) the cumene
20 hydroperoxide in the oxidation product.

[0023] In the oxidation reactor(s), the oxidation mixture is contacted with an oxygen-containing gas under oxidation conditions comprising an oxidation temperature effective to oxidize s-butylbenzene and (if present)
25 cumene, to produce the respective hydroperoxides. Suitable oxidation temperatures at most oxidation pressures are from about 90 °C to about 150 °C. Preferred temperatures will vary depending upon the type of oxidation reactor and the composition of the oxidation
30 feed. Conversion and selectivity to cumene hydroperoxide and s-butylbenzene hydroperoxide increases with an increase in the cumene:s-butylbenzene ratio in the oxidation feed. Conversion also increases with an increase in oxidation temperature.

35 [0024] In a batch oxidation reactor, the oxidation temperature can be adjusted throughout the reaction period to maximize selectivity of the oxidation reaction. Suitable oxidation pressures for batch reactor(s) are

from about 0 psig to about 100 psig, preferably from about 15 psig to about 40 psig.

[0025] In continuous oxidation reactor(s), the oxidation temperature in each oxidation reactor is selected to maximize selectivity, and will depend upon the composition of the oxidation feed. Suitable oxidation pressures when using continuous reactors generally are from about 0 psig to about 100 psig, preferably from about 15 psig to about 40 psig. Where the oxidation feed comprises a weight ratio of cumene:s-butylbenzene of 2:1, a preferred oxidation temperature for a continuous reactor is from about 100 °C to about 115 °C. Where the oxidation feed comprises a weight ratio of cumene:s-butylbenzene of 1:8, a preferred oxidation temperature for a continuous reactor is from about 110 °C to about 130 °C.

[0026] Oxidation reaction times will vary from about 5 to about 25 hours. The oxidation reaction time in a batch reactor preferably is from about 6 to about 11 hours for all cumene:s-butylbenzene ratios, with the oxidation temperature adjusted to maximize selectivity.

[0027] Where the oxidation reactor(s) are continuous oxidation reactors, the "reaction time" typically is referred to as the total residence time. The total residence time is divided between all of the continuous reactors used. For example, if 5 continuous oxidation reactors are operated in series, the residence time for each oxidation reactor is from about 1 to about 5 hours, with oxidation reaction temperatures for each continuous reactor chosen appropriately to achieve desired conversions. The total residence time can be distributed uniformly or non-uniformly between the oxidation reactors.

[0028] Both batch reactors and continuous oxidation reactors produce a total conversion of at least about 5% to the desired hydroperoxide, preferably at least s-butylbenzene hydroperoxide, also preferably comprising combined cumene hydroperoxide and s-butylbenzene

hydroperoxide. Preferably, total conversion is from about 10% to about 30%, more preferably from about 15% to about 25%.

5 [0029] When carrying out the reaction in multiple continuous reactors, any number of continuous reactors can be employed. Product selectivity is increased by increasing the number of continuous reactors. For example, using two continuous reactors produces a higher yield of the desired hydroperoxides than using only one
10 continuous reactor. In a preferred embodiment, from about 3 to about 8 continuous reactors are used in series. The preferred number of reactors will vary with the cumene:s-butylbenzene ratio of the oxidation feed. For example, where the oxidation feed comprises a ratio
15 of 2:1 cumene:s-butylbenzene, it is preferred to use 4 reactors. In contrast, where the oxidation feed comprises a ratio of 1:8 cumene:s-butylbenzene, it is preferred to use 5 or 6 reactors.

[0030] Where the oxidation reactor is one or more
20 continuous reactor(s), the continuous reactor(s) can be a variety of types, including but not necessarily limited to stirred tank reactor(s) or bubble column reactor(s).

[0031] When the oxidation reactor(s) are stirred tank reactor(s), oxidation feed addition and oxidation bottoms
25 withdrawal can be from any location. In a preferred embodiment, the oxidation feed is added in the impeller region of a stirred tank reactor(s). In stirred tank reactor(s), it is important to maximize bubble formation and total bubble surface area.

30 [0032] When the oxidation reactor(s) are bubble column reactor(s), the oxidation product is withdrawn from any location in the vessel, but preferably from the bottom of the vessel. Air preferably is added near the bottom of the bubble column reactor through a sparger designed to
35 produce bubbles of small size. The size of the bubbles suitably is about 10 mm or less, preferably 5 mm or less.

[0033] Typically, formic acid and acetic acid are produced as oxidation by-products as well as acetophenone (AP), dimethyl benzyl alcohol (DMBA), and ethyl methyl benzyl

alcohol (EMBA). Formic and acetic acids catalyze the formation of phenol, which is a poison (or inhibitor) of the main oxidation pathway to make the desired products. Formic and acetic acids, and hence phenol, cause a
5 reduction in the formation of desired products relative to by-products.

[0034] Although it is not necessary to use a neutralizing base (or "oxidation base") in the oxidation mixture, the yield of hydroperoxides is increased and attendant by-
10 product formation (e.g., AP, DMBA, EMBA) is decreased by the addition of small amounts of oxidation base. The use of an oxidation base also neutralizes acids, such as acetic and formic acid, as they are formed. In this way, the acids are prevented from forming phenol, and the yield
15 of desired hydroperoxide product is maximized.

[0035] Where oxidation base is used, it is preferred to add to the oxidation mixture a solution of oxidation base in an amount sufficient to neutralize the acids formed at the oxidation conditions. If oxidation base is used, it
20 is preferred to add a portion of the oxidation base separately to each oxidation reactor, most preferably to a series of continuous oxidation reactors.

[0036] The base solution preferably comprises a concentration of water which is sufficient to act as a
25 carrier for the oxidation base, but insufficient to cause separation of the oxidation mixture into an aqueous phase and an organic phase. The amount of water in the oxidation mixture preferably is from about 400 ppm to about 2 wt.%.

[0037] The oxidation base is added in an amount sufficient to produce a molar ratio of base to acids of from about
30 0:1 to about 6:1, preferably from about 0.5:1 to about 4:1. Suitable oxidation bases are those that have a pH of about 8 to about 12.5 in 1 to 10 wt.% aqueous solution and
35 include, but are not necessarily limited to alkali bases, anhydrous ammonia, and aqueous ammonia. Preferred alkali bases include, but are not necessarily limited to alkali metal carbonates and alkali metal bicarbonates. Suitable

alkali metals are potassium and sodium. A preferred alkali base is sodium carbonate.

[0038] Ammonia also is a preferred oxidation base. Ammonia can be added as gaseous anhydrous ammonia, as gaseous
5 anhydrous ammonia along with a small water feed, or as aqueous ammonia.

[0039] Without limiting the application to a particular mechanism of action, the small amount of water in the oxidation mixture is believed to improve the solubility of
10 the oxidation base in the oxidation mixture, making the oxidation base more readily available to perform the neutralization.

[0040] Oxidation is an exothermic reaction, and the heat of reaction is removed from the oxidation reaction
15 mixture during the reaction. For example, some heat is removed by vaporization of hydrocarbon, products and water, if water is present in the oxidation reaction mixture, into the air passing through the reactors, while most heat is removed by heat exchange between the
20 oxidation mixture and cooling fluids. Internal cooling coils can be employed in the oxidation reactors. Preferably, the oxidation reaction mixture is recirculated to heat exchangers external to the oxidation reactor(s).

[0041] The oxidation vapor overhead is passed through one or more stages of cooling, during which unreacted hydrocarbons and aqueous material, if present, are condensed and separated from each other. The hydrocarbons are recovered and recycled. The aqueous
30 material typically contains significant amounts of ethanol, methanol, ethyl hydroperoxide, and/or methyl hydroperoxide.

[0042] In a preferred embodiment, the oxidation vapor overhead is separated into an oxidation vapor overhead
35 organic fraction ("OVO-OF"), which may be recycled, and an oxidation vapor overhead "aqueous" fraction ("OVO-AF"). The OVO-AF is decomposed under thermal decomposition conditions effective to decompose ethyl hydroperoxide and methyl hydroperoxide, resulting in a

thermal decomposition product. The thermal decomposition product comprises alcohols, aldehydes, and/or carboxylic acids. The thermal decomposition conditions comprise a thermal decomposition temperature of from about 80°C to
5 250°C, more preferably from 150°C to 200°C, and a pressure of from about 100 psig to about 200 psig.

[0043] In one embodiment, the thermal decomposition conditions comprise adding an inorganic acid to the OVO-AF at a concentration effective to accelerate the
10 decomposition. Suitable inorganic acids include, but are not necessarily limited to sulfuric acid, hydrochloric acid, and phosphoric acid. For purposes of efficiency, a preferred inorganic acid is sulfuric acid, preferably concentrated sulfuric acid. The inorganic acid is added
15 to achieve a concentration of from about 20 ppm to about 100 ppm of the inorganic acid in the OVO-AF. After decomposition is complete, the inorganic acid is neutralized with an alkali base. Preferably, the alkali base has a pH of about 11 or less, even more preferably a
20 pH of from about 10 to about 11. Preferred bases are selected from the group consisting of sodium hydroxide and sodium carbonate.

[0044] The thermal decomposition product is subjected to distillation under thermal decomposition product
25 distillation conditions (TDP-distillation conditions) effective to produce a thermal decomposition product organic distillate (TDP-OD) and a thermal decomposition product "aqueous" bottoms (TDP-AB). The TDP-distillation conditions comprise a TDP-distillation temperature
30 effective to remove organic species other than carboxylic acids from the first decomposition product. The TDP-distillation suitably is carried out at atmospheric pressure.

[0045] The TDP-OD is disposed of as waste using
35 appropriate means.

Oxidation Product Separation Zone

[0046] Referring to Fig. 1, the oxidation bottoms (OB) and an amount of water is fed to an oxidation product

separation zone 12. Where no oxidation base is fed to the oxidation, a preferred oxidation product separation zone 12 is one or more strippers. The amount of water fed to the oxidation product separation zone 12 is
5 sufficient to recover methanol, ethanol, methyl hydroperoxide, and ethyl hydroperoxide in the first condenser vapor phase (described below). Generally, an amount of water equivalent to from about 0.1 wt.% to about 1.5 wt.% of the oxidation bottoms is sufficient.

10 **[0047]** When an oxidation base is fed to oxidation, a preferred oxidation product separation zone 12 is one or more washing decanters used to remove salts formed in the oxidation, followed by one or more strippers. In this embodiment, the oxidation product, water and/or base is
15 fed to the washing decanter(s). Salts in the oxidation product extract into the aqueous layer in the decanter. Some water dissolves in the oxidation product during the wash step. The amount of water dissolved in the oxidation product is sufficient to recover methanol,
20 ethanol, methyl hydroperoxide, and ethyl hydroperoxide in the first condenser vapor phase (described below).

[0048] In the one or more strippers, the OB is exposed to stripping conditions effective to concentrate, but ineffective to decompose s-butylbenzene hydroperoxide and
25 (if present) cumene hydroperoxide. The stripping conditions produce a stripper bottoms comprising s-butylbenzene hydroperoxide and (if cumene was fed to oxidation) cumene hydroperoxide and a stripper overhead comprising unreacted hydrocarbon, water, and organic
30 species having a boiling point lower than s-butylbenzene hydroperoxide and cumene hydroperoxide. Organic species removed in the stripper overhead include, but are not necessarily limited to the minor by-products delineated above, and small amounts of DMBA, EMBA, and acetophenone.
35 Typically, thermal decomposition of s-butylbenzene hydroperoxide and (if present) cumene hydroperoxide is minimized or avoided at stripper bottoms temperatures of less than 120 °C.

[0049] Although the use of a single stripper is encompassed by the present invention, a preferred embodiment involves feeding the OB through multiple strippers, more preferably through three strippers in sequence. In a preferred embodiment, the OB is fed through multiple strippers operated at sequentially decreasing pressures to produce a stripper overhead and a stripper bottoms. In this preferred embodiment, the stripping conditions comprise a bottoms temperature of 120 °C or less, preferably less than 120 °C, and: a first stripper pressure of from about 40 to about 60 mm Hg; a second stripper pressure of from about 25 to about 35 mm Hg; and, a third stripper pressure of from about 10 to about 20 mm Hg. In a most preferred embodiment: the first stripper conditions comprise a first stripper pressure of about 50 mm Hg; a second stripper pressure of about 30 mm Hg; and, a third stripper pressure of about 15 mm Hg. Greater than about 90 wt.% of the hydrocarbons in the OB are recycled back to the oxidation reactors.

[0050] In a preferred embodiment, the first stripper conditions are effective to produce a first stripper overhead comprising a portion of the cumene (if present) and a portion of the s-butylbenzene in the OB, 99 wt.% or more of the water fed with the OB, 99 wt.% or more of the methanol in the OB, 99 wt.% or more of the ethanol in the OB, 99 wt.% or more of the methyl hydroperoxide in the OB, and 99 wt.% or more of the ethyl hydroperoxide in the OB. In a most preferred embodiment, all of the water, all of the methanol, all of the ethanol, all of the methyl hydroperoxide, and all of the ethyl hydroperoxide in the OB is stripped overhead in the first stripper overhead.

[0051] The first stripper preferably comprises at least a first stripper overhead condenser, preferably a multiple first stripper overhead condenser system. The first stripper overhead condenser is operated under partial condensation conditions referred to herein as first stripper overhead condenser conditions. The first

stripper overhead condenser conditions comprise a first
stripper overhead condensation temperature and a first
stripper overhead condensation pressure effective to
cause a majority of the cumene (if present) and a
5 majority of the s-butylbenzene in the first stripper
overhead to condense, producing a first condenser organic
phase. Preferably, the first stripper overhead condenser
conditions are effective to condense about 90 wt.% or
more of the s-butylbenzene and about 85 wt.% or more of
10 the cumene (if present) in the first stripper overhead
into the first stripper overhead first condenser organic
phase. The first stripper overhead condenser conditions
also comprise a temperature and pressure effective to
produce a first condenser vapor phase comprising a
15 majority, preferably about 95 wt.% or more, of the water,
the ethanol, the methanol, the methyl hydroperoxide, and
the ethyl hydroperoxide in the first stripper overhead.
[0052] The first condenser vapor phase is separated from
the first condenser organic phase, and the first
20 condenser vapor phase is subjected to second condensation
conditions effective to form a second condenser organic
phase and a second condenser "aqueous" phase comprising a
majority, preferably about 90 wt.% or more, of the
ethanol, the methanol, the methyl hydroperoxide, and the
25 ethyl hydroperoxide in the first condenser vapor phase.
[0053] The second condenser aqueous phase is separated
from the second condenser organic phase, and the second
condenser aqueous phase is subjected to thermal
decomposition conditions effective to decompose methyl
30 hydroperoxide and ethyl hydroperoxide, producing a
thermal decomposition product comprising alcohols,
aldehydes, and/or carboxylic acids. The thermal
decomposition conditions are the same as described
previously for the thermal decomposition of the oxidation
35 vapor overhead aqueous fraction (OVO-AF). The second
condenser aqueous phase either is thermally decomposed
independently, or the OVO-AF and the second condenser
aqueous phase are combined to produce a decomposition

mixture which is exposed to the thermal decomposition conditions.

Cleavage Zone

5 [0054] The stripper bottoms comprising one or more of s-butylbenzene hydroperoxide and cumene hydroperoxide is fed to a cleavage zone 14 (Fig. 1). The cleavage zone 14 comprises one or more cleavage reactor(s) in which the stripper bottoms is subjected to a first cleavage reaction and a second cleavage reaction.

10 [0055] Where the oxidation feed comprises s-butylbenzene, the oxidation product generally comprises ethyl methyl benzyl carbinol (**EMBA**). A cumene oxidation product generally contains dimethylbenzyl alcohol (**DMBA**). It is desirable during cleavage to maximize conversion of DMBA
15 in the oxidation product to α -methyl styrene (AMS), and to maximize conversion of EMBA in the oxidation product to α -ethyl styrene (AES) and 2-phenyl-2-butene (2P2B) because these compounds can be hydrogenated to produce cumene and s-butylbenzene for recycle back to the
20 oxidation reactors, which increases overall conversion efficiency.

[0056] Unfortunately, many cleavage reactions are run at relatively high reaction temperatures. For example, the reaction temperature in typical boiling pot reactions is
25 from about 75 °C to about 85 °C. At such high reaction temperatures, significant amounts of DMBA, EMBA, product AMS, product AES, and product 2P2B are converted to "non-recoverable by-products." The present application provides a process for cleaving one or more
30 hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof to reduce the production of non-recoverable by-products of DMBA and EMBA.

[0057] The cleavage reaction feed to the cleavage zone 14
35 generally is the stripper bottoms, water, and a ketone stream selected from the group consisting of an acetone stream, an MEK stream, or a mixed acetone/MEK stream. The stripper bottoms comprises hydroperoxides selected

from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. It has been found that the feed from the MEK recovery zone is an aid in reducing production of non-recoverable by-products from DMBA and/or EMBA. Water in the amount of 0.5% to 2% of the weight of the remainder of the feed is added to moderate the reaction.

5 [0058] When the cleavage reaction occurs in a single reactor, the cleavage reaction feed is first exposed to first cleavage reaction conditions (described below) comprising a relatively low temperature, and subsequently exposed to second cleavage reaction conditions (also described below) in the same reactor. In a preferred embodiment, the stripper bottoms is a first cleavage reactor feed 32 (Fig. 2) to a first cleavage reactor 15.

10 [0059] The cleavage reactor(s) may be a variety of reactor types. Preferred reactors include, but are not necessarily limited to plug-flow reactors ("PFR's"); plug-flow reactors with recycle (PFRR's); and continuous stirred tank reactors (CSTR's).

15 [0060] The first cleavage reactor 15 can be a stirred tank reactor with associated internal or external heat exchange equipment effective to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. In a preferred embodiment the first cleavage reactor 15 is a pipeline loop reactor comprising one or more heat exchangers 20, 22 at appropriate locations to provide cooling sufficient to maintain the first cleavage reaction mixture at the first cleavage reaction temperature. Generally, the first cleavage reaction temperature is from about 45°C to about 70°C. In a preferred embodiment, the first cleavage reaction temperature is from about 45°C to about 60°C, more preferably from about 45°C to about 55°C. The first cleavage reaction pressure is maintained sufficiently high to maintain the first cleavage reaction mixture in the liquid phase. Operating at about 0.5 atmospheres or

more generally is sufficient to maintain the first cleavage reaction mixture in the liquid phase.

[0061] A pump 24 is installed in the pipeline loop to provide for recirculation of a recycle flow of the first cleavage reaction mixture through the first cleavage reactor 15. A second portion of the first cleavage reaction mixture, the "first cleavage reaction product," is withdrawn from the pipeline loop reactor at a withdrawal point 26 located a short distance upstream of the feed point 28 for the first cleavage reactor feed 32. The recycle flow 30 through the pipeline loop of the first cleavage reactor 15 is much larger than the flow of the first cleavage reactor feed 32 (sometimes referred to as the "first cleavage reactor feed flow 32"). Preferably, the ratio of the recycle flow 30 to the first cleavage reactor feed flow 32 is from about 10:1 to about 100:1 on a weight basis, and more preferably from about 20:1 to 40:1 on a weight basis.

[0062] The first cleavage reaction conditions comprise a first cleavage reaction residence time effective to cleave from about 95% to about 98% of hydroperoxides selected from the group consisting of s-butylbenzene hydroperoxide, cumene hydroperoxide, and combinations thereof. Depending upon the hydroperoxides present in the first cleavage reaction mixture, the hydroperoxides are converted to phenol and a compound selected from the group consisting of methyl ethyl ketone (MEK), acetone, and combinations thereof. Generally, the first cleavage reaction residence time is from about 1 minute to about 10 minutes.

[0063] The first cleavage reaction conditions comprise an acid catalyst effective to catalyze the cleavage of s-butylbenzene hydroperoxide and (if present) cumene hydroperoxide. Suitable acid catalysts include, but are not necessarily limited to sulfuric acid, sulfuric acid anhydride, perchloric acid, and phosphoric acid. A preferred acid catalyst is sulfuric acid. In a preferred embodiment, the acid catalyst (preferably concentrated sulfuric acid), is added to a reaction mixture side